

(12) UK Patent Application (19) GB (11) 2 306 689 (13) A

(43) Date of A Publication 07.05.1997

(21) Application No 9622638.6

(22) Date of Filing 30.10.1996

(30) Priority Data

(31) 07305102	(32) 30.10.1995	(33) JP
07394373	28.12.1995	
08140782	10.05.1996	

(51) INT CL⁵
B41N 1/24(52) UK CL (Edition O)
G2C CHX CH8A5 CH6B3 CH6D1(58) Documents Cited
GB 2176621 A EP 0647533 A EP 0542930 A
EP 0542929 A EP 0592215 A WO 95/13824 A(71) Applicant(s)
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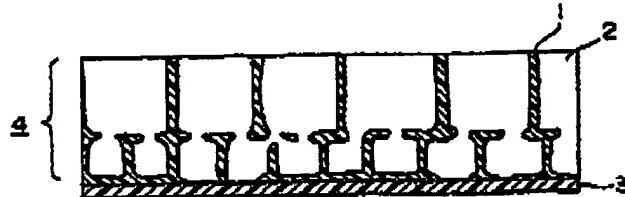
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UK CL (Edition O) G2C CHX
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(74) continued overleaf

(54) Heat sensitive stencil

(57) A heat-sensitive stencil comprising a thermoplastic film (3) and a porous resin layer (4) with pores (2) and walls (1). The stencil has an air permeability from 1.0 to 157 cm³/cm²*sec when the thermoplastic resin film of the portion is perforated to provide an open ratio S_o/S_p of at least 0.2, wherein S_o represents the area of the perforations and S_p represents the total area. The film is preferably 0.5 to 10μm thick and the layer preferably has pores of diameter 2 to 50μm and a thickness of 5 to 100μm and there is preferably a backing layer of a silicone resin and an antistatic agent. The heat-sensitive stencil is prepared by applying to the film a coating liquid containing the resin and a mixture of a good solvent and a poor solvent less vaporizable than the good solvent and drying so that the porous resin layer is formed. Alternatively, the resin is dissolved in the good solvent and the coating liquid applied to the film and then sprayed with the bad solvent to form the porous layer or drying.

FIG. 2



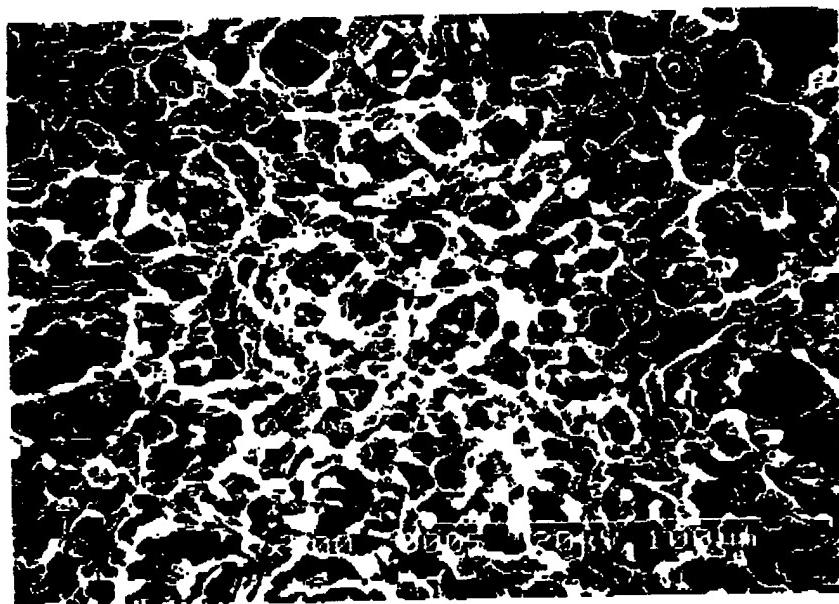
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FIG. 2

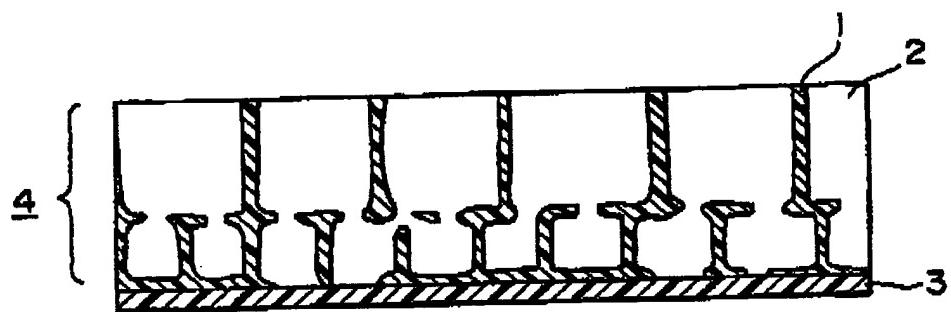
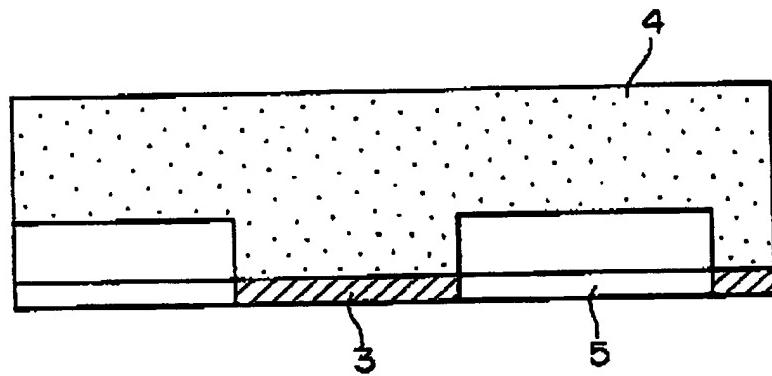
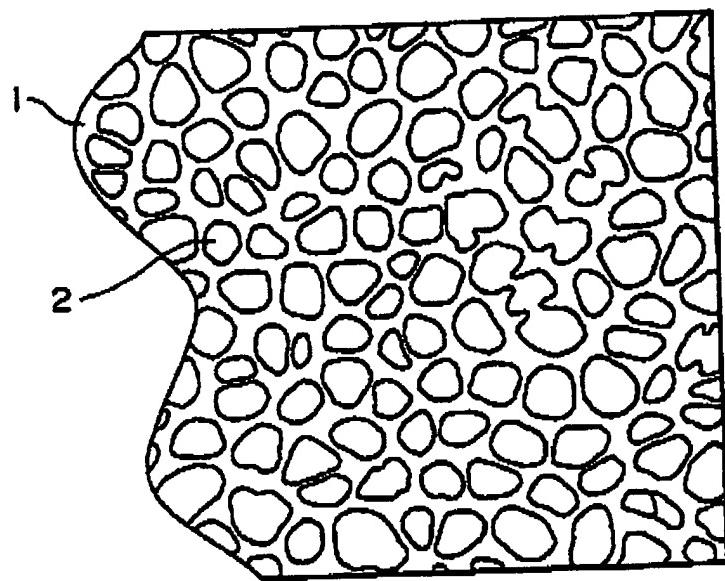


FIG. 3

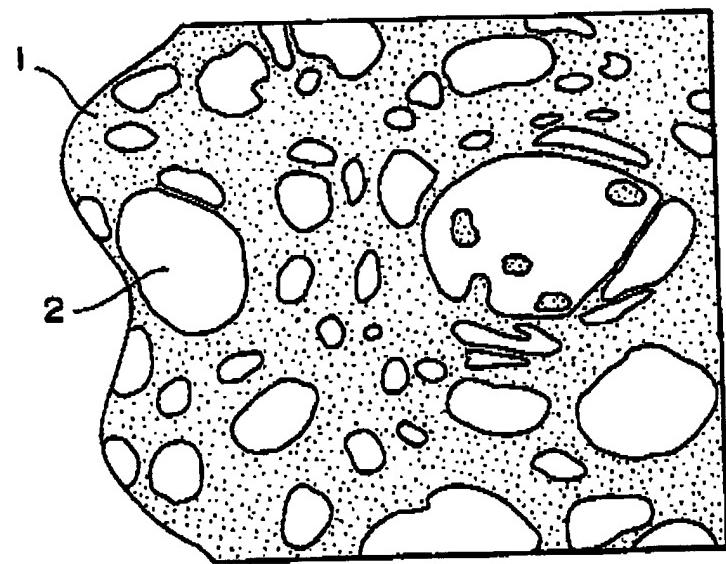


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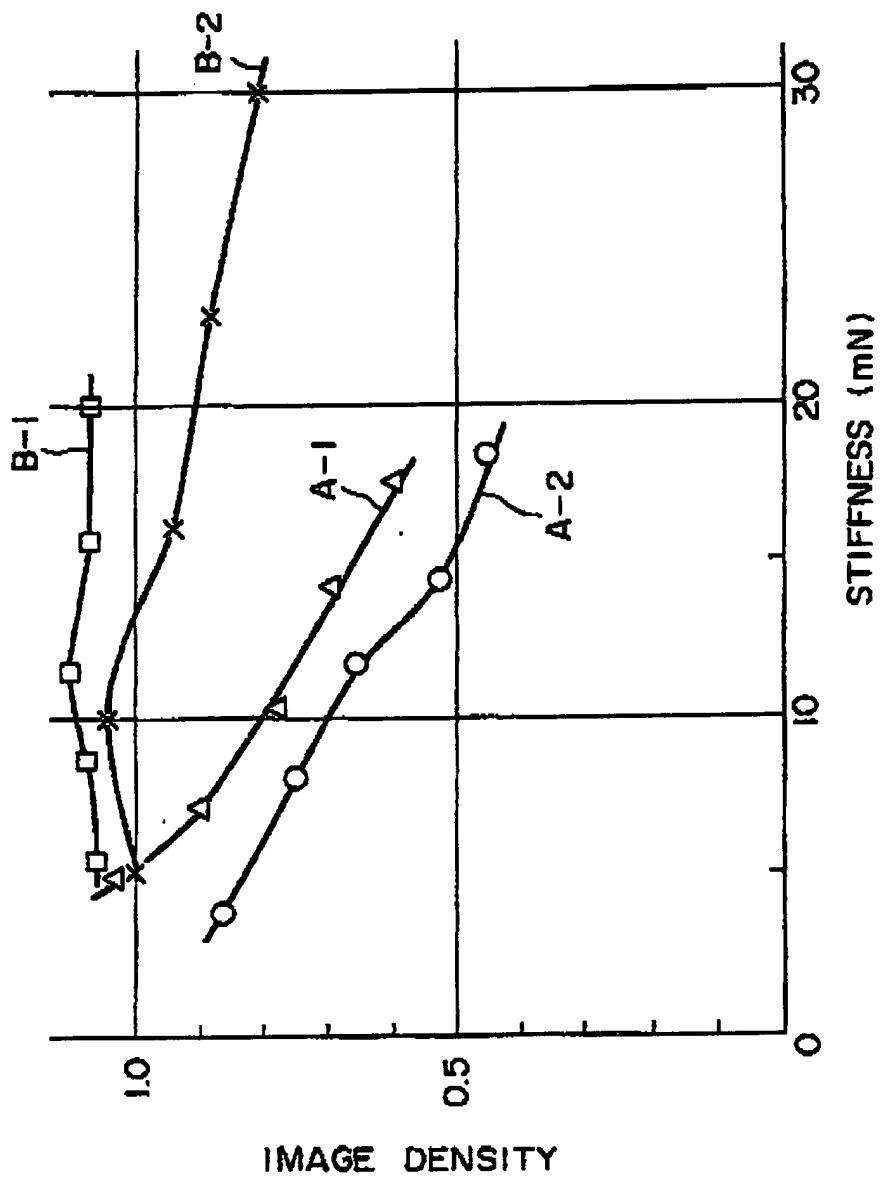


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FIG. 6



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2306689Title of the Invention**HEAT-SENSITIVE STENCIL AND METHOD OF FABRICATING SAME**Background of the Invention

This invention relates to a heat-sensitive stencil and to a method of fabricating same.

One known heat-sensitive stencil is composed of an ink-permeable thin paper serving as an ink support and a thermoplastic resin film bonded with an adhesive to the support. The stencil is heated imagewise by, for example, a thermal head to perforate the heated portions of the thermoplastic resin film, thereby obtaining a printing master for reproducing images by mimeographic printing. The conventional stencil, however, poses problems because (1) the adhesive tends to be accumulated in interstices between fibers to form "fins" which prevent the thermal perforation during the master forming step and the passage of an ink during the printing step, (2) the fibers per se prevent smooth passage of an ink and (3) the paper support is relatively expensive.

To cope with the above problems, JP-A-54-33117 proposes a stencil having no paper support and composed substantially only of a thermoplastic resin film. While this stencil can completely solve the above-mentioned problems, a new serious problem arises; i.e. it is necessary to significantly increase the thickness of the stencil in order to obtain satisfactory stiffness required for transferring the stencil master during printing stage. An increase of the thickness results in the lowering of the thermal sensitivity.

JP-A 61-198459 discloses a method of fabricating a stencil wherein a multiplicity of closed patterns such as circular patterns are formed by gravure printing of a radiation-curable heat-resisting resin on a thermoplastic resin film, followed by curing. Since this method unavoidably gives patterns have a thickness of 50 µm or more,

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the formation of perforations with a thermal head is not easy. Further, ink stains are apt to be formed on prints obtained using such a stencil master.

5 Summary of the Invention

It is, therefore, an object of the present invention to provide a heat-sensitive stencil having satisfactory stiffness and excellent sensitivity to thermal perforation.

10 Another object of the present invention is to provide a heat-sensitive stencil without an adhesive and paper.

15 It is a further object of the present invention to provide a heat-sensitive stencil of the above-mentioned type which can give a printing master capable of producing uniform, clear printings even with a small amount of an ink.

20 It is yet a further object of the present invention to provide a heat-sensitive stencil of the above-mentioned type which can give a printing master capable of producing printed images free of ink blurs and stains.

25 It is a further object of the present invention to provide a method which can easily fabricate a heat-sensitive stencil.

30 In accomplishing the foregoing objects, there is provided in accordance with one aspect of the present invention a heat-sensitive stencil comprising a thermoplastic resin film, and a porous resin layer formed thereon, said stencil having an air permeability in the range of 1.0 $\text{cm}^3/\text{cm}^2 \cdot \text{sec}$ to 157 $\text{cm}^3/\text{cm}^2 \cdot \text{sec}$ in a portion thereof when said thermoplastic resin film of said portion is perforated to form perforations providing an open ratio S_o/S_p of at least 0.2, wherein S_o represents a total area of said perforations and S_p represents the area of said portion.

35 The provision of the porous layer can impart satisfactory stiffness to the stencil without adversely

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affecting the sensitivity to perforation thereof.

The air permeability of a printing master has been found to represent the ink permeability thereof. An air permeability of a printing master of below $1.0 \text{ cm}^3/\text{cm}^2 \cdot \text{sec}$ even with an open ratio S_0/S_1 of 1.0 means that the porous resin layer has a low porosity and that the master has poor ink permeability. On the other hand, an air permeability in excess of $157 \text{ cm}^3/\text{cm}^2 \cdot \text{sec}$ means that the porous resin layer has poor ink retentivity so that stains and blurs are apt to be formed.

In another aspect, the present invention provides a method of preparing a heat-sensitive stencil, comprising the steps of:

- (a) dissolving a resin in a mixed solvent including a first solvent capable of dissolving said resin, and a second solvent substantially incapable of dissolving said resin and having an evaporation rate lower than that of said first solvent, thereby to obtain a coating liquid;
- (b) applying said coating liquid over a surface of a thermoplastic resin film to form a resin coating; and
- (c) heating said resin coating to dryness.

The present invention also provides a method of preparing a heat-sensitive stencil, comprising the steps of:

- (a) applying a solution of a resin in a first solvent over a surface of a thermoplastic resin film to form a wet resin coating over said surface;

- (b) spraying vapors or fine droplets of a second solvent substantially incapable of dissolving said resin over said wet resin coating so that said second solvent is taken into said wet resin coating to cause a portion of said resin to precipitate; and

- (c) heating said resin coating to dryness.

Brief Description of the Drawings

Other objects, features and advantages of the

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present invention will become apparent from the detailed description of the preferred embodiments of the invention which follows, when considered in light of the accompanying drawings, in which:

5 Fig. 1 is an electron microphotograph of a porous resin layer of a heat-sensitive stencil according to the present invention;

10 Fig. 2 is a sectional view schematically illustrating a heat-sensitive stencil according to the present invention;

15 Fig. 3 is a sectional view schematically illustrating a state of a heat-sensitive stencil according to the present invention where perforations have been formed;

Fig. 4 and 5 are enlarged view schematically illustrating the openings in the surfaces of heat-sensitive stencils prepared in Examples 1 and 10, respectively; and

20 Fig. 6 is a graph showing a relationship between image density and flexural rigidity of heat-sensitive stencils according to the present invention.

Detailed Description of the Preferred Embodiments of the Invention

The heat-sensitive stencil according to the present invention has a porous resin layer serving as an ink support and formed on a thermoplastic resin film. The stencil is adapted show an air permeability in the range of 1.0 cm³/cm²·sec to 157 cm³/cm²·sec, preferably 10 cm³/cm²·sec to 80 cm³/cm²·sec, in a portion thereof when the thermoplastic resin film of that portion is perforated to form perforations providing an open ratio S₁/S₂ of at least 0.2, wherein S₁ represents a total area of the perforations and S₂ represents the area of the portion.

25 The air permeability may be measured in the following manner. A square solid pattern (black pattern) with a size of 10 x 10 cm is read by a printer (PRIFORT VT

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3820 manufactured by Ricoh Company, Ltd.) and a sample stencil is perforated with a thermal head in accordance with the read out pattern to form a printing master. The perforation operations are performed for five similar samples so that five printing masters having open ratios S_o/S_p of about 0.2, 0.35, 0.50, 0.65 and 0.80 are obtained. The open ratio of a master may be measured by making a photomicrograph (magnification: 100) thereof. The photomicrograph is then magnification-copied (magnifying ratio: 200) using a copying machine (IMAGIO MF530 manufactured by Ricoh Company, Ltd.). Perforations shown in the copy are marked on an OHP film and then read by a scanner (300 DPI, 256 gradient). This is binarized with an image retouch software Adobe Photoshop 2.5J. The open ratio of the perforations is measured using an image analysis software NIH IMAGE. The perforated portion of each of the printing masters is measured for the air permeability thereof by any conventional method. When at least one of the five masters has an air permeability in the range of $1.0 \text{ cm}^3/\text{cm}^2 \cdot \text{sec}$ to $157 \text{ cm}^3/\text{cm}^2 \cdot \text{sec}$, the stencil is regarded as falling within the scope of the present invention.

Fig. 1 is an electron microphotograph of an example of a porous resin layer. A plurality of pores of an open cellular structure are present. Fig. 2 is a sectional view schematically illustrating one embodiment of a stencil according to the present invention. Designated as 3 is a thermoplastic resin film on which a porous resin layer 4 having pores 2 defined by resin walls 1 is formed.

The porous layer 4 preferably has an average pore diameter of 2-50 μm , more preferably 5-30 μm , for reasons of proper ink permeability.

It is preferred that the total area S_p of the openings of the porous resin layer 4 having an equivalent diameter of at least 5 μm , preferably 5-50 μm , be 4-80 %, more preferably 10-60 %, of a total area S of the surface of

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the porous resin layer 4 for reasons of proper ink passage therethrough and proper capability of the formation of perforations. The term "openings" herein refers to pores 2 exposed to a surface of the layer 4 and the term "equivalent diameter" refers to a diameter of a circle having the same area as that of the corresponding "opening". The total area of the openings may be measured from an electron microphotograph (magnification: 1,000) of the surface of the porous layer 4. The photograph is processed by an image processor (LA-555D manufactured by Pierce Inc.) for determining the diameter of the circle corresponding to the opening.

It is also preferred that the total area of the openings having an equivalent diameter of at least 5 μm , preferably 5-50 μm , is at least 50 % of a total area of the openings for reasons of proper ink passage therethrough and proper capability of the formation of perforations.

The porous resin layer 4 preferably has a thickness of 5-100 μm , more preferably 6-50 μm , for reasons of proper stiffness of the stencil and proper ink transference. The density of the porous resin layer 4 is preferably 0.01-1 g/cm³, more preferably 0.1-0.7 g/cm³, for reasons of proper stiffness and mechanical strengths.

For reasons of proper transferability of the printing master in the printer, it is preferred that the stencil has a flexural rigidity of 5-200 mN, more preferably 10-50 mN, when measured with a Lorentzen Stiffness Tester.

Any resin may be used for the formation of the porous layer 4. Illustrative of suitable resins of the porous layer 4 are a vinyl resin such as polyvinyl chloride), poly(vinyl butyral), vinyl chloride-vinyl acetate copolymer, vinyl chloride-vinylidene chloride copolymer or vinyl chloride-acrylonitrile copolymer; a polyamide such as nylon; polybutylene; polyphenylene oxide; (meth)acrylic ester; polycarbonate; or a cellulose derivative such as

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5 acetylcellulose, acetylbutylcellulose or acetylpropylcellulose. These resins may be used singly or in combination of two or more. It is preferred that the porous resin layer 4 contain a resin capable of softening at a temperature at which the perforation by a thermal head is carried out, generally at a temperature of 150°C or less, for reasons of facilitating the perforation of the thermoplastic resin film 3.

10 The porous resin layer 4 can contain one or more additives such as a filler, an antistatic agent, a stick-preventing agent, a surfactant, an antiseptic agent and an antifoaming agent. Addition of a filler to the porous resin layer 4 is desirable to control the strength, stiffness and the size of pores thereof. Use of a filler in the form of 15 needles or plates is particularly preferred. Illustrative of suitable fillers are needle-like natural mineral fillers such as magnesium silicate, sepiolite, potassium titanate, wollastonite, zonolite and gypsum fiber; needle-like synthetic mineral fillers such as non-oxide-type needle whiskers, oxide whiskers and mixed oxide whiskers; platy fillers such as mica, glass flakes and talc; and pigments such as poly(vinyl chloride) particles, poly(vinyl acetate) 20 particles, polymethyl acrylate particles, zinc oxide, titania, calcium carbonate and microcapsules (e.g. Matsumoto Microsphere). The filler is generally used in an amount of 25 8-20 % based on the weight of the resin of the porous resin layer.

30 Any thermoplastic resin conventionally used in heat-sensitive stencil master may be used for the film 3. Illustrative of suitable thermoplastic resins are vinyl chloride-vinylidene chloride copolymers, polypropylene and polyesters. A polyester film having melting energy of 3-11 cal/g (JP-A-62-149496), a polyester film having a degree of crystallization of 30 % or less (JP-A-62-28173) and a 35 polyester film containing at least 5% mol% of butylene

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terephthalate units (JP-A-2-158391) are particularly preferred because they permit perforation with a low energy. The thermoplastic resin film 3 preferably has a thickness of 0.5-10 µm, more preferably 1-5 µm for reasons of easiness in formation of the porous layer 4 thereon and in formation of perforations.

If desired, the thermoplastic resin layer 3 may be backed by a stick preventing layer (not shown) containing a stick preventing agent such as a silicone mold release agent, a fluorine resin mold release agent or a phosphoric ester surfactant.

Fig. 3 schematically illustrate the state where the stencil has been processed by a thermal head to form perforations 5. In the illustrated case, the thermoplastic resin layer 3 is perforated with part of the porous resin layer 4 in each of the perforations 5 remaining unremoved and covering the perforations 5. The remaining portion of the porous resin layer 4 serves to control the amount of ink transferred from the master to a paper during the mimeographic printing stage. Such remaining portion of the layer 4 can be formed by suitably adjusting the thickness of the layer 4.

One preferred method (first embodiment) of fabricating the above heat-sensitive stencil will be next described. A resin for forming the porous resin layer 4 is first dissolved, completely or partly, in a mixed solvent including a first solvent (good solvent) capable of dissolving the resin and a second solvent (poor solvent) substantially incapable of dissolving the resin and having a lower evaporation rate than the first solvent, thereby to obtain a coating liquid in the form of a solution or a dispersion. Preferably the second solvent has a boiling point which is higher by 10-40°C than that of the first solvent and which is preferably 150°C or less.

The concentration of the resin in the mixed solvent

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solution is generally 2-50 % by weight, preferably 5-30 % by weight. The weight ratio of the first solvent to the second solvent, which has an influence upon the pore structure of the porous resin layer 4, is generally 40:60 to 95:5.

5 The thus obtained coating liquid is then applied over a surface of a thermoplastic resin film to form a wet resin coating. The application of the coating liquid may be carried out by any desired coating method such as blade coating, transfer roll coating, wire bar coating, reverse roll coating or gravure coating. In this case, it is preferred that the coating liquid immediately before being applied be heated at a temperature higher than that of the atmosphere at which the coating step is performed and which is generally room temperature. Thus, when the coating is 10 performed with a die coater, the die from which the solution is applied to the thermoplastic resin film may be surrounded by a heating jacket to which a heating medium is fed. It is also preferred that coating liquid immediately after being applied to the thermoplastic resin film be cooled before the 15 next drying step to a temperature lower by 2-30°C, preferably 5-20°C, than that of the coating liquid immediately before 20 being applied.

The wet resin coating is then heated at a temperature below the boiling point of the second solvent but sufficient to vaporize part of the first solvent so that a portion of the resin precipitates. Subsequently, the coating is further heated preferably at 80°C or less until the coating is completely dried. During the course of the vaporization of the solvents, there are formed a multiplicity 30 of pores.

Examples of suitable poor and good solvents are shown in Table 1 below. As shown, good and poor solvents vary with the resin to be dissolved.



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Table 1

	Resin	PVC*1	VCA*2	PB*3	PS*4	ANS*5	ABS*6
	Solvent (b.p. °C)						
5	Methanol(64.5)	poor	poor	poor	poor	poor	poor
	Ethanol(78.3)	poor	poor	poor	-	-	poor
	Ethyl acetate(77.1)	-	good	poor	good	good	-
	Acetone(56.1)	good	good	poor	good	good	good
10	Methyl ethyl ketone(79.6)	good	good	poor	good	good	good
	Diethyl ether(34.5)	poor	-	-	poor	poor	poor
	Tetrahydrofuran (65-67)	good	good	good	good	-	-
	Hexane(68.7)	poor	poor	good	poor	poor	-
15	Heptane(98.4)	poor	poor	poor	poor	poor	poor
	Benzene(80.1)	-	poor	good	good	good	good
	Toluene(110.6)	-	good	good	good	good	good
	Xylene(139.1)	-	good	good	good	good	good
	Chloroform(61.2)	-	good	good	good	good	good
20	Carbon tetrachloride(76.7)	-	good	good	good	-	-
	Water(100.0)	poor	poor	poor	poor	poor	poor

*1 PVC: poly(vinyl chloride)

25 *2 VCA: vinyl chloride-vinyl acetate copolymer

*3 PB: polybutylene

*4 PS: polystyrene

*5 ANS: acrylonitrile-styrene copolymer

*6 ABS: acrylonitrile-butadiene-styrene copolymer

30 *7 MAR: methacrylic acid resin

*8 PVA: poly(vinyl acetate)

*9 PC: polycarbonate

*10 AC: acetylcellulose resin

*11 AR: acrylate resin

35 *12 WB: polyvinyl-butylal

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Table 1 (continued)

	Resin	MAR*7	PVA*8	PC*9	AC*10	AR*11	VB*12
	Solvent(b.p. °C)						
5	Methanol(64.5)	-	good	poor	-	poor	good
	Ethanol(78.3)	-	poor	poor	-	poor	good
	Ethyl acetate(77.1)	good	good	poor	good	good	good
	Acetone(56.1)	good	good	poor	good	good	good
10	Methyl ethyl ketone(79.6)	good	good	poor	good	-	good
	Diethyl ether(34.5)	-	poor	-	-	-	poor
	Tetrahydrofuran (65-67)	good	-	good	good	-	good
15	Hexane(68.7)	poor	poor	poor	poor	poor	poor
	Heptane(98.4)	poor	poor	poor	poor	poor	poor
	Benzene(80.1)	good	good	good	-	good	poor
	Toluene(110.6)	good	good	good	poor	good	poor
20	Xylene(139.1)	good	good	good	poor	good	-
	Chloroform(61.2)	good	good	good	good	good	-
	Carbon tetrachloride(76.7)	-	-	good	poor	-	-
	Water(100.0)	poor	poor	poor	poor	poor	poor

In a second embodiment, the heat-sensitive stencil according to the present invention may be prepared as follows. First, a solution of a resin for the porous resin layer in a first solvent is prepared. The solution is applied over a surface of a thermoplastic resin film to form a wet resin coating over the surface. Then, vapors or fine droplets of a second solvent substantially incapable of dissolving the resin are sprayed over the wet resin coating so that the second solvent is taken into the wet resin coating to cause a portion of the resin to precipitate. Thereafter, the resin coating is heated to dryness. The first and second solvents are similar to those described

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above. In the second embodiment, the size and number of pores may be controlled by the amount and particle size of the droplets of the second solvent. It is preferred that the thermoplastic resin film be previously applied with a spray of the second solvent before being applied with the solvent solution of the resin, since the contact area between the resulting porous resin layer and the thermoplastic resin film is decreased and, therefore, the stencil can be more easily perforated by a thermal head.

If desired, the above first and second methods may be combined for the fabrication of the stencil according to the present invention.

The following examples will further illustrate the present invention. Parts are by weight.

Example 1

Polyvinyl-butylal (softening point: 87°C)	4 parts
Ethanol (b.p. 78.3°C)	35.5 parts
Water (b.p. 100.0°C)	11.5 parts

The above composition was stirred to dissolve the resin in the mixed solvent and allowed to quiescently stand to remove foams. The solution was then uniformly applied to a biaxially stretched polyester film (thickness: 3.5 µm) with a wire bar at a temperature of 30°C and a relative humidity of 90 %, thereby to form a wet coating having a deposition amount of 7.0 g/cm² (on dry basis). This was allowed to stand as such for 1 minute and then placed in a drying chamber at 50°C for 2 minutes to dry the coating. The dried coating was a porous layer whose surface was as illustrated in Fig. 4. A liquid containing a silicone resin and a cationic antistatic agent was applied on the back side of the polyester film opposite the porous layer and dried to form a stick preventing layer having a deposition amount of 0.05 g/m², thereby obtaining a heat-sensitive stencil A-1 according to

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the present invention.

Example 2

A heat-sensitive stencil A-2 was prepared in the same manner as described in Example 1 except that the following composition was substituted for that of Example 1.

Polyvinyl-acetal	4 parts
Ethanol (b.p. 78.3°C)	36 parts
Water (b.p. 100.0°C)	26 parts

10

Example 3

Cellulose acetate butyrate (softening point: 83°C)	3 parts
Methyl ethyl ketone (b.p. 79.6°C)	85 parts

15

The above composition was stirred to dissolve the resin in the solvent and allowed to quiescently stand to remove foams. The solution was then uniformly applied to a biaxially stretched polyester film (thickness: 3.5 µm) with a wire bar at a temperature of 30°C and a relative humidity of 90 %, thereby to form a wet coating having a deposition amount of 7.0 g/cm² (on dry basis). Fine droplets of water were sprayed for 15 seconds from Humidiffer UV-107D (manufactured by Hitachi Inc.) over the surface of the wet coating placed at a distance 10 cm away from the Humidiffer. This was allowed to stand as such for 1 minute and then placed in a drying chamber at 50°C for 2 minutes to dry the coating. The dried coating was a porous layer. A liquid containing a silicone resin and a cationic antistatic agent was applied on the back side of the polyester film opposite the porous layer and dried to form a stick preventing layer having a deposition amount of 0.05 g/m², thereby obtaining a heat-sensitive stencil A-3 according to the present invention.

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Example 4

A heat-sensitive stencil A-4 was prepared in the same manner as described in Example 3 except that the following composition was substituted for that of Example 3.

5 Vinyl chloride-vinyl acetate copolymer

(softening point: 83°C) 3 parts

Methyl ethyl ketone (b.p. 79.6°C) 17 parts

Methanol (b.p. 64.5°C) 9 parts

10 **Example 5**

Polyvinyl-butyral (softening point: 87°C) 4 parts

Methanol (b.p. 64.5°C) 33.6 parts

Water (b.p. 100.0°C) 2.8 parts

15 The above composition was stirred to dissolve the resin in the mixed solvent and allowed to quiescently stand to remove foams. The resin solution was then uniformly applied to a biaxially stretched polyester film (thickness: 2.0 µm) with a wire bar at a temperature of 20°C, thereby to form a wet coating having a deposition amount of 7.0 g/cm² (on dry basis). This was allowed to stand as such for 15 seconds and then placed in a drying chamber at 50°C for 1 minute to dry the coating. The dried coating was a porous layer. A liquid containing a silicone resin and a cationic antistatic agent was applied on the back side of the polyester film opposite the porous layer and dried to form a stick preventing layer having a deposition amount of 0.05 g/m², thereby obtaining a heat-sensitive stencil A-5 according to the present invention. During the coating of the resin solution, the temperature on the surface of the polyester film was measured with a thermometer (Digital Surface Thermometer Type E manufactured by Anritsu Inc.). The results are shown below:

30 Temperature of the atmosphere in which
 the coating was carried out: 20°C

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Temperature of the resin solution immediately before application:	20°C
Temperature of the resin solution on the film immediately after application:	17°C^*
* temperature drop due to evaporation of the solvent	

Example 6

10 Example 5 was repeated in the same manner as described except that the application of the resin solution onto the polyester film was carried out using a die coater equipped with a heating jacket under the conditions shown below, thereby obtaining a heat-sensitive stencil A-6.

15 Temperature of the atmosphere in which the coating was carried out:	20°C
Temperature of the resin solution immediately before application:	25°C
Temperature of the resin solution on the film immediately after application:	22°C^*
* temperature drop due to evaporation of the solvent	

25 Example 7

Polyvinyl-butyral (softening point: 87°C)	4 parts
Ethanol (b.p. 78.3°C)	35.5 parts
Water (b.p. 100.0°C)	11.5 parts
Needle-like magnesium silicate	0.8 part

30 The above composition was mixed with a ball mill to obtain a dispersion. The dispersion was then uniformly applied to a biaxially stretched polyester film (thickness: 1.5 μm) with a wire bar, thereby to form a wet coating having a deposition amount of 7.0 g/cm^2 (on dry basis). This was

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placed in a drying chamber at 50°C for 3 minutes to dry the coating. The dried coating was a porous layer. A liquid containing a silicone resin and a cationic antistatic agent was applied on the back side of the polyester film opposite the porous layer and dried to form a stick preventing layer having a deposition amount of 0.05 g/m², thereby obtaining a heat-sensitive stencil B-1 according to the present invention.

10 Example 8

A heat-sensitive stencil B-2 was prepared in the same manner as described in Example 7 except that the following composition was substituted for that of Example 7.

	Polyvinyl-acetal	4 parts
15	Ethanol (b.p. 78.3°C)	36 parts
	Water (b.p. 100.0°C)	26 parts
	Platy magnesium silicate (talc)	0.8 part

20 Example 9

A heat-sensitive stencil B-3 was prepared in the same manner as described in Example 7 except that the following composition was substituted for that of Example 7.

	Polycarbonate	4 parts
	Polyvinyl-butyral	2.2 parts
25	Tetrahydrofuran	56 parts
	Ethanol (b.p. 78.3°C)	7.6 parts
	Potassium titanate whisker	0.8 part

30 Example 1C

A heat-sensitive stencil B-4 was prepared in the same manner as described in Example 7 except that the following composition was substituted for that of Example 7. The surface of the porous resin layer of the stencil B-4 is illustrated in Fig. 5.

35 Vinyl chloride-vinyl acetate copolymer

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	(softening point: 78°C)	3 parts
	Sepiolite	4 parts
	Acetone (b.p. 56.1°C)	20 parts
	Ethanol (b.p. 78.3°C)	8 parts

5

Example 11

A heat-sensitive stencil B-5 was prepared in the same manner as described in Example 7 except that the following composition was substituted for that of Example 7.

10	Cellulose acetate butylate (softening point: 152°C)	3 parts
	Acetone (b.p. 56.1°C)	20 parts
	Water (b.p. 100.0°C)	5 parts
	Silica powder	0.3 part

15

Example 12

A heat-sensitive stencil B-6 was prepared in the same manner as described in Example 7 except that the following composition was substituted for that of Example 7.

20	Polyvinyl-butylal (softening point: 87°C)	4 parts
	Ethanol (b.p. 78.3°C)	24.5 parts
	Water (b.p. 100.0°C)	11.5 parts
	Acrylic acid-styrene copolymer (softening point: 65°C)	0.6 part
25	Titanium oxide (rutile)	0.8 part

Comparative Example 1

30	Cellulose acetate butylate (softening point: 131°C)	15 parts
	Methyl ethyl ketone (b.p. 79.5°C)	5 parts

The above composition was stirred to dissolve the resin in the solvent and allowed to quiescently stand to remove foams. The solution was then uniformly applied to a biaxially stretched polyester film (thickness: 3.5 µm) with a

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wire bar at a temperature of 20°C and a relative humidity of 60 %, thereby to form a wet coating. This was allowed to stand as such for 1 minute and then placed in a drying chamber at 50°C for 2 minutes to dry the coating. A liquid containing a silicone resin and a cationic antistatic agent was applied on the back side of the polyester film opposite the dried layer and dried to form a stick preventing layer having a deposition amount of 0.05 g/m², thereby obtaining a heat-sensitive stencil C-1.

10

Comparative Example 2

A paper formed of natural jute (Manila hemp) fibers and synthetic fibers was bonded with an adhesive to a biaxially stretched polyester film (thickness: 3.5 μm), thereby obtaining a heat-sensitive stencil C-2.

15

Comparative Example 3

A heat-sensitive stencil C-3 was prepared in the same manner as described in Comparative Example 1 except that the following composition was substituted for that of Comparative Example 1.

Acrylic acid-styrene copolymer

(O/W emulsion; resin content: 43 %;

softening point: 47°C)

16 parts

25

Water (b.p. 100.0°C)

33 parts

Colloidal silica (average particle

diameter: 0.015 μm)

3 parts

Comparative Example 4

A liquid containing a silicone resin and a cationic antistatic agent was applied on one side of a biaxially stretched polyester film (thickness: 3.5 μm) and dried to form a stick preventing layer having a deposition amount of 0.05 g/m², thereby obtaining a heat-sensitive stencil C-4.

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Comparative Example 5

A liquid containing a silicone resin and a cationic antistatic agent was applied on one side of a biaxially stretched polyester film (thickness: 7.0 μm) and dried to form a stick preventing layer having a deposition amount of 0.05 g/ m^2 , thereby obtaining a heat-sensitive stencil C-5.

Each of the heat-sensitive stencils A-1 to A-6, B-1 to B-6 and C-1 to C-5 was measured for (a) the air permeability at various open ratios S_0/S_p of 0.2-0.8 (S_0 and S_p are as defined previously), (b) percentage S_1 of the total area of the openings having an equivalent diameter of at least 5 μm relative to a total area of the surface of the porous resin layer, and (c) percentage S_2 of the total area of the openings having an equivalent diameter of at least 5 μm relative to a total area of the openings in the manner described previously. The results are summarized in Table 2.

Table 2

Stencil	S_0/S_p (%)	Air Permeability ($\text{cm}^3/\text{cm}^2 \cdot \text{sec}$)	S_1 (%)	S_2 (%)
A-1	21	15	47	73
	32	32		
	48	50		
	63	65		
A-2	78	82		
	22	3	3	38
	35	8		
	51	14		
	66	24		
A-3	81	34		
	20	4	85	45
	37	9		
	45	14		
	63	20		
	77	26		

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Table 2 (continued)

	Stencil	S_0/S_p (%)	Air Permeability	S_1 (%)	S_2 (%)
			($\text{cm}^3/\text{cm}^2 \cdot \text{sec}$)		
5	A-4	20	136	2	53
		26	140		
		45	152		
		58	163		
		78	175		
10	A-5	23	19	52	89
		38	26		
		53	34		
		67	46		
		83	53		
15	A-6	21	9	58	93
		38	18		
		52	28		
		67	37		
		82	46		
20	B-1	24	23	53	78
		32	34		
		46	42		
		69	72		
		87	85		
25	B-2	22	0.3	2	41
		34	2.4		
		51	4		
		66	8		
		82	14		
30	B-3	21	124	15	95
		36	142		
		51	164		
		66	183		
		82	200		

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Table 2 (continued)

	Stencil	S_0/S_p (%)	Air Permeability ($\text{cm}^3/\text{cm}^2 \cdot \text{sec}$)	S_1 (%)	S_2 (%)
5	B-4	21	134	3	58
		38	147		
		52	155		
		67	167		
		81	177		
10	B-5	24	6	87	44
		45	10		
		53	15		
		68	22		
		83	28		
15	B-6	20	43	60	99
		32	49		
		45	56		
		62	62		
		77	70		
20	C-1	30	0.8	0	0
	C-2	50	220		
	C-3	10	0.05		
	C-4	25	300		
	C-5	-	-		

25

Each of the heat-sensitive stencils A-1 to A-6, B-1 to B-6 and C-1 to C-5 was further measured for bonding strength, flexural rigidity, perforation sensitivity, print uniformity and ink stain. The test results are summarized in Table 3 and the test methods are shown below. The preparation of printing masters and mimeographic printing using same in these tests were carried out using a commercially available printer (VT3820 manufactured by Ricoh Company Ltd.) and an ink (VT600 II manufactured by Ricoh Company Ltd., viscosity at 20°C: 153 poise).

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Bonding strength

Bonding strength between the thermoplastic resin film and the support (porous resin layer in the case of the present invention) is measured by perforating a sample stencil with a thermal head to see whether or not the support is separated from the thermoplastic resin film. Evaluation is made according to the following ratings:

- 5 A: no separation
- 10 B: slight separation
- C: significant separation

Flexural rigidity

Flexural rigidity is measured with Lorentzen Stiffness Tester. A stencil having a flexural rigidity of less than 5 mN is ill-suited for actual use.

15 Perforation sensitivity

A sample stencil is subjected to perforation with a thermal head. Perforation sensitivity is evaluated according to the following ratings:

- 20 A: completely normally perforated
- B: completely perforated but diameters are reduced
- C: not completely perforated
- D: hardly perforated

25 Print Uniformity

Prints obtained using sample stencils are compared with those obtained using a commercially available stencil (VT2 Master manufactured by Ricoh Company Ltd.) with respect to absence of blurs and of density variation. Evaluation is made according to the following ratings:

- 30 A: much superior
- B: slightly better
- C: comparable
- D: inferior

35 Ink Stain

Prints obtained using sample stencils are compared

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with those obtained using a commercially available stencil (VT2 Master manufactured by Ricoh Company Ltd.) with respect to absence of ink stains on both sides thereof. Evaluation is made according to the following ratings:

5

- A: much superior
- B: slightly better
- C: comparable
- D: inferior

10

Table 3

	Stencil	Bonding Strength	Flexural Rigidity	Perforation Sensitivity	Print Uniformity	Ink Stain
			(mN)			
15	A-1	B	15	B	B	B
	A-2	B	16	C	C	A
	A-3	B	16	B	C	B
	A-4	A	19	C	B	C
	A-5	A	19	A	A	A
20	A-6	A	17	A	A	A
	B-1	B	28	B	B	B
	B-2	B	30	C	C	A
	B-3	B	34	C	B	C
	B-4	A	28	C	B	C
25	B-5	A	32	B	C	B
	B-6	A	29	A	A	A
	C-1	A	10	B	D	-
	C-2	A	90	D	C	D
	C-3	B	4	C	D	-
30	C-4	B	-	A	C	C
	C-5	B	6	D	D	-

No porous resin layer is formed in stencil of comparative examples. In the case of stencil C-5, the fill was too thick to be perforated. The stencil C-4 had so small stiffness that it was difficult to automatically transfer the

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stencil in the printer.

Example 13

5 Examples 1 and 2 were repeated in the same manner as described except that the deposition amount of the porous resin layer was varied. Each stencil was perforated and subjected to mimeographic printing and also measured for the flexural rigidity. The relationship between flexural rigidity and image density is shown in Fig. 6. The curves A-1 and A-2 are the results of the variation of Examples 1
10 and 2, respectively.

Example 14

15 Examples 7 and 8 were repeated in the same manner as described except that the amount of the filler was varied. Each stencil was perforated and subjected to mimeographic printing and also measured for the flexural rigidity. The relationship between flexural rigidity and image density is shown in Fig. 6. The curves B-1 and B-2 are the results of
20 the variation of Examples 7 and 8, respectively.

25 As will be appreciated from the results shown in Fig. 6, the image density is little changed by increasing the stiffness by increasing the amount of the filler. On the other hand, the image density decreases by increasing the stiffness by increasing the thickness of the porous resin layer.

30 The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all the changes which come within the meaning and range of equivalency of the claims are therefore
35 intended to be embraced therein.

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What Is Claimed Is:

1. A heat-sensitive stencil comprising a thermoplastic resin film, and a porous resin layer formed thereon, said stencil having an air permeability in the range of 1.0 cm³/cm²·sec to 157 cm³/cm²·sec in a portion thereof when said thermoplastic resin film of said portion is perforated to form perforations providing an open ratio S_o/S_p of at least 0.2, wherein S_o represents a total area of said perforations and S_p represents the area of said portion.

2. A heat-sensitive stencil as claimed in claim 1, wherein said porous resin layer has pores exposed to a surface thereof to form a multiplicity of openings, wherein at least part of said openings has an equivalent diameter of at least 5 µm, said equivalent diameter being defined as a diameter of a circle having the same area as that of the corresponding opening, and wherein the total area of said openings having an equivalent diameter of at least 5 µm is 4-80 % of a total area of said surface of said porous resin layer.

3. A heat-sensitive stencil as claimed in claim 1, wherein said porous resin layer has pores exposed to a surface thereof to form a multiplicity of openings, wherein at least part of said openings has an equivalent diameter of at least 5 µm, said equivalent diameter being defined as a diameter of a circle having the same area as that of the corresponding opening, and wherein the total area of said openings having an equivalent diameter of at least 5 µm is at least 50 % of a total area of said openings.

4. A heat-sensitive stencil as claimed in claim 1, wherein said porous resin layer contains a filler.

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5. A heat-sensitive stencil as claimed in claim 4,
wherein said filler is in the form of needles or plates.

5 6. A heat-sensitive stencil as claimed in claim 1, and
having a flexural rigidity of 5-200 mN.

10 7. A heat-sensitive stencil as claimed in claim 1,
wherein said porous resin film includes a resin having a
softening point of 150°C or less.

15 8. A heat-sensitive stencil as claimed in claim 1,
wherein said porous resin layer has such a thickness that,
when said thermoplastic resin film is perforated to form
perforations providing an open ratio S_o/S_p , where S_o and S_p are
as defined above, of 0.2-0.8, at least part of said porous
resin layer in each of said perforations remains
unperforated.

20 9. A method of preparing a heat-sensitive stencil,
comprising the steps of:

25 (a) dissolving a resin in a mixed solvent including
a first solvent capable of dissolving said resin, and a
second solvent substantially incapable of dissolving said
resin and having an evaporation rate lower than that of said
first solvent, thereby to obtain a coating liquid;

(b) applying said coating liquid over a surface of
a thermoplastic resin film to form a resin coating; and

(c) heating said resin coating to dryness.

30 10. A method as claimed in claim 9, wherein said
coating liquid immediately before being applied is heated at
a temperature higher than that of the atmosphere at which
step (b) is performed.

35 11. A method as claimed in claim 9, wherein said

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coating liquid immediately after being applied is cooled before step (c).

12. A method of preparing a heat-sensitive stencil,
5 comprising the steps of:

(a) applying a solution of a resin in a first solvent over a surface of a thermoplastic resin film to form a wet resin coating over said surface;

10 (b) spraying vapors or fine droplets of a second solvent substantially incapable of dissolving said resin over said wet resin coating so that said second solvent is taken into said wet resin coating to cause a portion of said resin to precipitate; and

(c) heating said resin coating to dryness.

15 13. A method as claimed in claim 12, wherein said second solvent has an evaporation rate lower than that of said first solvent.

20 14. A method as claimed in claim 12, wherein said second solvent is water or an aqueous alcohol.

25 15. A heat-sensitive stencil comprising a thermoplastic resin film having a thickness of 0.5-10 µm, and a porous resin layer formed on said thermoplastic resin film and having an open cellular structure, said porous resin layer having pores with an average pore diameter of 2-50 µm, a thickness of 5-100 µm and a density of 0.1-1 g/cm³.

30 16. A heat-sensitive stencil as claimed in claim 15, wherein said porous resin layer contains a filler.

17. A heat-sensitive stencil as claimed in claim 15, wherein said filler is in the form of needles or plates.

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18. A heat sensitive stencil as claimed in claim 15, and having a flexural rigidity of 5-200 mN.

19. A heat-sensitive stencil as claimed in claim 15, wherein said porous resin layer includes a resin having a softening point of 150°C or less.

20. A heat-sensitive stencil, substantially as herein described with reference to the accompanying drawings and examples.

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21. A method of preparing a heat-sensitive stencil, substantially as herein described with reference to the accompanying drawings and examples.

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The
Patent
Office

29

Application No: GB 9622638.6
Claims searched: 1-21

Examiner: Meredith Reynolds
Date of search: 21 January 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): G2C(CHX)

Int Cl (Ed.6): B41N

Other:

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB2176621A (Asia Stencil)(Page 1 lines 81-115)	I and 15 at least
X	EP0647533A (Toray)(Pages 3-5,Exs)	--
X	EP0642930A (Riso)(Page 3 lines 14-24,Exs 1-2)	--
X	EPO642929A (")(Page 3, Ex 3)	--
X	EP0592215A (")(Exs, esp. Ex 3)	--
X	WO95/13924 (Toray)(Page 4 and Exs)	--
<i>(X CP C 673ct)</i>		

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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